

Appl. No. 10/657,585

Amendment and Response dated June 22, 2006

Reply to Office Action of March 29, 2006

Amendments to the Claims

This listing of claims will replace all prior versions, and listings, of claims in the application:

Listing of Claims:

1. (Currently amended) A method of making a catalyst support comprising
 - a) applying at least one compound of a rare-earth metal to an aluminum-comprising material to provide a rare-earth metal modified alumina precursor;
 - b) drying the rare-earth metal modified alumina precursor under suitable conditions to provide a dried rare-earth metal modified alumina precursor; and
 - c) calcining the dried rare-earth metal modified alumina precursor in a manner effective for converting at least a portion of the aluminum-comprising material to an alumina comprising at least one alumina phase selected from the group consisting of delta-alumina, theta-alumina, and combination thereof; and
creating a surface coverage comprising an oxide of said at least one rare-earth metal, wherein said surface coverage coats the alumina at least partially, and wherein at least one rare-earth metal is essentially trivalent, and further wherein the surface coverage is between about 0.2 nm and about 0.5 nm in thickness.
2. (Original) The method according to claim 1 wherein the aluminum-comprising material comprises at least one material selected from the group consisting of aluminum oxides, aluminum salts, aluminum alkoxides, aluminum hydroxides, pseudoboehmite, boehmite, gibbsite, bayerite, gamma-alumina, theta-alumina, delta-alumina, eta-alumina, rho-alumina, chi-alumina, kappa-alumina and any combinations thereof.
3. (Original) The method according to claim 1 wherein the aluminum-comprising material comprises a gamma-alumina.
4. (Original) The method according to claim 3 wherein the gamma-alumina has a surface

Appl. No. 10/657,585

Amendment and Response dated June 22, 2006

Reply to Office Action of March 29, 2006

area between about 100 m²/g and about 300 m²/g; and a pore volume of at least about 0.2 ml/g.

5. (Original) The method according to claim 3 wherein the gamma-alumina comprises no more than about 0.1% by weight Na₂O.
6. (Original) The method according to claim 1 wherein the compound of the rare-earth metal comprises a counterion selected from the group consisting of nitrate, acetate, oxalate, acetylacetonate, any alkanoate, any halide and sulfate.
7. (Original) The method according to claim 6 wherein the compound of the rare-earth metal is in a hydrated form.
8. (Original) The method according to claim 1 wherein the rare-earth metal is selected from the group consisting of yttrium, lanthanum, praseodymium, neodymium, samarium and gadolinium.
9. (Original) The method according to claim 1 wherein applying a compound of the rare-earth metal is carried out by an impregnation technique.
10. (Original) The method according to claim 9 wherein the impregnation technique is performed at about or below ambient pressure.
11. (Original) The method according to claim 9 wherein the impregnation technique is incipient wetness impregnation.
12. (Canceled)
13. (Original) The method according to claim 1 wherein calcining is effective for creating a rare-earth metal oxide surface layer that completely covers the alumina surface.

Appl. No. 10/657,585
Amendment and Response dated June 22, 2006
Reply to Office Action of March 29, 2006

14. (Original) The method according to claim 1 wherein calcining is effective for converting at least a portion of the aluminum-comprising material to a transition alumina comprising theta-alumina.

15. (Original) The method according to claim 1 wherein calcining is performed at a temperature between about 800 °C and about 1,400 °C.

16. (Original) The method according to claim 15 wherein calcining is performed at a temperature between about 1,000 °C and about 1,300 °C.

17. (Original) The method of making a catalyst support according to claim 1 further comprising applying at least one compound of another rare-earth metal.

18. (Original) The method according to claim 17 wherein the application of at least one compound of another rare-earth metal is performed simultaneously to step a).

19. (Original) The method according to claim 17 wherein the application of at least one compound of another rare-earth metal is performed after step c).

20. (Original) The method according to claim 19 further comprising calcining at a temperature between about 300 °C and 900 °C.

21-31. (Canceled)

32. (Currently amended) A Fischer-Tropsch catalyst comprising
at least one catalytically active metal comprising cobalt, wherein the cobalt metal is
dispersed in crystallites having an average size of between about 5 nm and about 20 nm;
optionally, at least one promoter; and

Appl. No. 10/657,585
Amendment and Response dated June 22, 2006
Reply to Office Action of March 29, 2006

a rare-earth metal oxide modified catalyst support including
at least one alumina material comprising an alumina phase selected from the group consisting of delta-alumina, theta-alumina, and combination thereof; and optionally gamma-alumina; and
a surface coverage comprising an oxide of at least one rare-earth metal, wherein said coverage coats the alumina material at least partially, and wherein the at least one rare-earth metal is essentially trivalent.

33. (Canceled)

34. (Original) The catalyst of claim 32 wherein the catalytically active metal is present in an amount between about 1% and about 50% by weight of metal to final weight of catalyst.

35. (Original) The catalyst of claim 32 wherein the promoter comprises one element from Groups 1-14 of the Periodic Table of Elements.

36. (Canceled)

37. (Previously presented) The catalyst of claim 32 wherein the promoter comprises at least one metal selected from the group consisting of platinum, palladium, silver, ruthenium, iridium, rhodium, and rhenium.

38. (Previously presented) The catalyst of claim 32 wherein the cobalt metal is dispersed in crystallites arranged on the surface coverage comprising at least one trivalent rare-earth metal oxide.

39-41. (Canceled)

42. (Original) The catalyst according to claim 32 wherein the trivalent rare-earth metal is

Appl. No. 10/657,585
Amendment and Response dated June 22, 2006
Reply to Office Action of March 29, 2006

selected from the group consisting of yttrium, lanthanum, praseodymium, neodymium, samarium and gadolinium.

43. (Currently amended) The catalyst of claim 32 wherein the rare-earth metal oxide modified catalyst support further comprises a structural modifier, and said structural modifier comprises one element selected from the group consisting of boron, magnesium, silicon, calcium, titanium, chromium, manganese, iron, cobalt, nickel, copper, zinc, gallium, strontium, zirconium, molybdenum, tin, and barium.

44. (Currently amended) The ~~Fischer-Tropsch~~ catalyst according to claim 32 wherein the ~~Fischer-Tropsch~~ catalyst is used to practice any process for converting a reactant gas mixture comprising synthesis gas under suitable conditions to a product mixture comprising linear hydrocarbons.

45. (Currently amended) The ~~Fischer-Tropsch~~ catalyst according to claim 44 wherein the conditions suitable for converting a reactant gas mixture comprise a temperature no less than 160 °C and a pressure no less than about 5 atm.

46. (Currently amended) The ~~Fischer-Tropsch~~ catalyst according to claim 45 further comprising no more than about 10 mol% aluminate spinels comprising the catalytically active metal before, during or after said process.

47. (Currently amended) The ~~Fischer-Tropsch~~ catalyst according to claim 45 wherein the alumina that comprises the support retains its original phase upon exposure to said process.

48. (Currently amended) The ~~Fischer-Tropsch~~ catalyst according to claim 45 wherein the promoter retains a majority of its original activity upon exposure to said process.

Appl. No. 10/657,585
Amendment and Response dated June 22, 2006
Reply to Office Action of March 29, 2006

49. (Currently amended) A method of making a Fischer-Tropsch catalyst comprising applying at least one compound of a catalytically active metal to a rare-earth metal oxide modified catalyst support to form a catalyst precursor, wherein the rare-earth metal oxide modified catalyst support includes
- at least one alumina material comprising an alumina phase selected from the group consisting of theta-alumina, delta-alumina, eta-alumina, rho-alumina, chi-alumina, kappa-alumina, and any combinations thereof; and optionally gamma-alumina; and
 - a surface coverage comprising an oxide of at least one rare-earth metal, wherein said coverage coats the alumina material at least partially, and wherein the at least one rare-earth metal is essentially trivalent;
 - calcining said catalyst precursor; and
 - reducing calcined catalyst precursor to form a reduced catalyst; and further embedding the reduced catalyst in oil or solid hydrocarbon.
50. (Canceled)
51. (Original) The method of claim 49 wherein the trivalent rare-earth metal is selected from the group consisting of yttrium, lanthanum, praseodymium, neodymium, samarium and gadolinium.
52. (Currently amended) The method of claim 51 wherein the rare-earth metal oxide modified catalyst support comprises between about 1 wt% and about 15 wt% of rare-earth metal.
53. (Currently amended) The method of claim 49 wherein the rare-earth metal oxide modified catalyst support comprises an alumina phase containing essentially theta-alumina.
54. (Currently amended) The method of claim 49 wherein applying at least one compound of a catalytically active metal is done by impregnation.

Appl. No. 10/657,585
Amendment and Response dated June 22, 2006
Reply to Office Action of March 29, 2006

55. (Original) The method of claim 49 wherein the catalytically active metal comprises cobalt.
56. (Original) The method of claim 55 wherein the catalyst comprises between about 5 and about 40% cobalt.
57. (Original) The method of claim 55 wherein the compound of the catalytically active metal comprises cobalt nitrate, cobalt nitrate hexahydrate, cobalt acetate, cobalt acetylacetonate, or combinations thereof.
58. (Original) The method of claim 49 wherein the catalytically active metal comprises iron.
59. (Original) The method of claim 49 further comprising applying a compound of a promoter.
60. (Original) The method of claim 59 wherein the compounds of catalytically active metal and of the promoter are applying simultaneously by impregnation.
61. (Original) The method of claim 59 wherein the catalytically active metal is cobalt and the promoter comprises at least one metal selected from the group consisting of platinum, palladium, silver, ruthenium, iridium, rhodium, and rhenium.
62. (Original) The catalyst of claim 59 wherein the catalytically active metal is iron, and the promoter comprises at least one metal selected from the group consisting of sodium, copper, potassium, lithium, and silver.

Appl. No. 10/657,585

Amendment and Response dated June 22, 2006

Reply to Office Action of March 29, 2006

63. (Currently amended) A process for converting synthesis gas to hydrocarbons, wherein the process comprises

converting a reactant gas mixture comprising hydrogen and carbon monoxide under conditions effective for producing a product mixture comprising waxy paraffinic hydrocarbons over a hydrocarbon synthesis catalyst comprising

at least one catalytically active metal comprising cobalt, wherein the cobalt metal is dispersed in crystallites having an average size of between about 5 nm and about 20 nm;

optionally, at least one promoter; and

a rare-earth metal oxide modified catalyst support comprising

an alumina material comprising optionally gamma-alumina, and at least one alumina phase selected from the group consisting of delta-alumina, theta-alumina, and any combinations thereof; and

a surface coverage comprising at least one rare-earth metal oxide, wherein the at least one rare-earth metal is essentially trivalent, and wherein said coverage coats the alumina material at least partially.

64. (Original) The process according to claim 63 wherein the reactant gas mixture has a H₂:CO ratio between 0.67:1 and 5:1.

65. (Original) The process according to claim 63 wherein the reactant gas mixture has a H₂:CO ratio between 1.4:1 and 2.3:1.

66. (Previously presented) The process according to claim 63 wherein the waxy paraffinic hydrocarbons comprise linear hydrocarbons having at least 18 carbon atoms.

67. (Currently amended) The process according to claim 63 wherein the process ~~has a selectivity for hydrocarbon products characterized by~~ produces a hydrocarbon mixture having an alpha value of at least 0.85.

Appl. No. 10/657,585
Amendment and Response dated June 22, 2006
Reply to Office Action of March 29, 2006

68. (Original) The process according to claim 63 wherein the process produces methane and has a methane selectivity not more than about 10 wt%.

69. (Original) The process according to claim 63 wherein the waxy hydrocarbons contain no more than 100 ppm of catalytically active metal.

70. (Canceled)

71. (Currently amended) The process of claim ~~70~~ 63 wherein the catalytically active metal is cobalt, and the hydrocarbon synthesis catalyst further comprises a promoter, and further wherein said promoter comprises at least one metal selected from the group consisting of platinum, palladium, silver, ruthenium, iridium, rhodium, and rhenium.

72-73. (Canceled)

74. (Original) The process according to claim 63 wherein the rare-earth metal is selected from the group consisting of yttrium, lanthanum, praseodymium, neodymium, samarium and gadolinium.

75. (Currently amended) The process according to claim 63 wherein the rare-earth metal oxide modified catalyst support comprises between about 1 wt% and about 15 wt% of rare-earth metal.

76. (Previously presented) The catalyst of claim 32 wherein the catalyst comprises between about 5 and about 40% cobalt.

77. (Previously presented) The method of claim 55 wherein the cobalt metal is dispersed in crystallites having an average size of between about 1 nm and about 20 nm.

Appl. No. 10/657,585
Amendment and Response dated June 22, 2006
Reply to Office Action of March 29, 2006

78. (Previously presented) The method of claim 55 wherein the cobalt metal is dispersed in crystallites having an average size of between about 5 nm and about 20 nm.
79. (New) The catalyst according to Claim 32 wherein the catalyst comprises between about 15% and about 35% by weight of cobalt to final weight of catalyst.
80. (New) The catalyst according to Claim 32 wherein the trivalent rare-earth metal is present in an amount between about 1% and about 15% by weight of metal to final weight of modified support.
81. (New) The catalyst according to Claim 32 wherein the at least one rare-earth metal is present in an amount between about 3% and about 10% by weight of metal based on the final weight of the modified support.
82. (New) The catalyst according to Claim 32 wherein the trivalent rare-earth metal is selected from the group consisting of lanthanum, praseodymium and neodymium.
83. (New) The catalyst according to Claim 32 wherein the rare-earth metal oxide modified catalyst support has a surface area between about 40 m²/g and about 150 m²/g; and a pore volume between about 0.1 cm³/g and about 0.5 cm³/g.
84. (New) The catalyst according to Claim 32 wherein the rare-earth metal oxide modified catalyst support has a surface area between about 70 m²/g and about 130 m²/g.
85. (New) The catalyst according to Claim 32 wherein the surface coverage coats the alumina material completely.
86. (New) The catalyst according to Claim 32 wherein the surface coverage has a thickness of

Appl. No. 10/657,585
Amendment and Response dated June 22, 2006
Reply to Office Action of March 29, 2006

at least about 0.2 nanometer.

87. (New) The catalyst according to Claim 32 wherein the surface coverage is between about 0.2 nm and about 0.5 nm in thickness.

88. (New) The process according to Claim 32 wherein the rare-earth metal oxide modified catalyst support comprises at least 20% delta-alumina; at least 20% theta-alumina; or at least 20% of combined delta-theta-alumina.

89. (New) The process according to Claim 32 wherein the rare-earth metal oxide modified catalyst support comprises at least 20% theta-alumina.

90. (New) The process according to Claim 32 wherein the catalyst is in the form of particles which are embedded in oil or solid hydrocarbon.

91. (New) The process according to Claim 63 wherein the trivalent rare-earth metal is present in an amount between about 3% and about 10% by weight of rare-earth metal to final weight of modified support.

92. (New) The process according to Claim 63 wherein the catalyst comprises between about 15% and about 35% by weight of cobalt to final weight of catalyst.

93. (New) The process according to Claim 63 wherein the rare-earth metal oxide modified catalyst support comprises at least 20% theta-alumina.

94. (New) The process according to Claim 63 wherein the rare-earth metal oxide modified catalyst support has a surface area between about 40 m²/g and about 150 m²/g; and a pore volume between about 0.1 cm³/g and about 0.5 cm³/g.

Appl. No. 10/657,585
Amendment and Response dated June 22, 2006
Reply to Office Action of March 29, 2006

95. (New) The process according to Claim 63 wherein the catalyst further comprising no more than about 10 mol% aluminate spinels comprising the catalytically active metal before, during or after said process.

96. (New) The process according to Claim 63 wherein the catalyst is essentially free of aluminate spinels comprising the catalytically active metal before said process or during said process or both.